



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

Subject: PP# 7E3473, SO₂ on Grapes; Chilean Exporters' Association Submissions of January 25 and February 21, 1989; Stability Studies of Spiking Solutions; Monier-Williams Experiments, Radiotracer Studies; Chilean Grapes, Report on the SO₂ Analysis Results of the ELAPs Program, 1987-1988 (MRID Nos. 409816-01, 409816-02, 409816-03, 409816-04, 410092-01, DEB No. 5013).

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The Chilean Exporters' Association, representing Imal Ltda., Quimica Osku, Ltda. and Frupac International Corporation, has submitted the following reports in support of PP# 7E3473:

- Stability Studies of Spiking Solutions
- Monier-Williams Experiments, FDA Method Validation, Part 1: Radiotracer Studies
- Monier-Williams Experiments, FDA Method Validation, Part 2: Experimental Batch Records
- Monier-Williams Experiments, FDA Method Validation, Part 3: Experimental Batch Records
- Chilean Grapes, Report on the SO₂ Analysis Results of the Expedited Laboratory Analysis Procedures (ELAPs) Program, 1987-1988, Volume 1---Data Analysis

These data are submitted in response to our reviews of July 29, 1987 (PP# 7E3474, Experimental Protocols for Methodology and Metabolic Studies on the Use and Determination of Sulfur Compounds in Grapes, E.T. Haeberer) and September 22, 1988 (Sulfur Dioxide on Grapes; Data from Chilean Certification Program).

A tolerance for the residues of Sulfur Dioxide in/on grapes has been established at 10 ppm.

Recommendations

DEB recommends that the petitioner address the questions raised in Conclusions 1, 2, 4 and 5.

Deficiencies Remaining

In conjunction with the establishment of a tolerance for the residues of Sulfur Dioxide on grapes at 10 ppm, the petitioner has agreed to submit a radiolabeled metabolism study for Sulfur Dioxide on grapes. This study remains outstanding.

Conclusions

1. The report titled "Stability Studies of Spiking Solutions" appears to be a copy of laboratory notebook data tables. No discussion or explanation of the material is provided. A written review and explanation of the data is needed.
2. The report titled "Monier-Williams Experiments FDA Method Validation Part 1: Radiotracer Studies" requires additional clarification. The section from page 24 through page 39 is difficult to interpret.
3. The questions raised in the DEB review of September 22, 1988, "Sulfur Dioxide on Grapes; Data from Chilean Certification Program" (Elizabeth T. Haeberer), have been adequately addressed.
4. A comparison of recoveries obtained with different grape types and colors has not been included. The registrant refers to inclusion of these data in Exhibit 3, however, Exhibit 3 was not included in this report.
5. In conjunction with the establishment of a tolerance for the residues of SO_2 on grapes at 10 ppm, the petitioner has agreed to submit a radiolabeled metabolism study for SO_2 on grapes. This study remains outstanding.

Detailed Considerations

The current data address questions raised in the two reviews cited above and will be discussed in chronological order.

The submission on experimental protocols for methodology and metabolic studies, which was reviewed July 29, 1987, was divided into two sections:

1. Validation of the FDA-Modified Monier-Williams Method
2. Metabolic Studies of Sulfur Dioxide in Grapes

The current submission addresses the first section and the petitioner has indicated that the second section, i.e., metabolism study of SO₂ in grapes, will be addressed at a later date.

The protocol described a study to determine the stability of various spiking reagents, both stabilized and unstabilized, under varying conditions. The report titled "Stability Studies of Spiking Solutions" (MRID# 409816-01) appears to be a copy of hand-written laboratory notes and tables. No discussion or explanation is provided. No conclusions can be drawn from these data. A clarification of the intent of the experiments is needed as well as a written summary of the results.

The petitioner also proposed an S-35 radiotracer study to identify and quantitate system losses in the modified Monier-Williams analysis. The report "Monier-Williams Experiments FDA Method Validation Part 1: Radiotracer Studies" (MRID# 409816-02) is intended to satisfy this proposal. DER has been unable to draw a conclusion concerning the adequacy of this study due to difficulty in understanding the narrative portion of the report from page 24 through 39 inclusive. A clarification of the report will be needed.

In response to the conclusions in the September 22, 1988 DER review "Sulfur Dioxide on Grapes; Data From Chilean Certification Program" (Elizabeth T. Haebeler), the petitioner has submitted the report "Chilean Grapes, Report on the SO₂ Analysis Results of the Expedited Laboratory Analysis Procedures (ELAPs) Program, 1987-1988, Volume 1---Data Analysis." The questions raised in the conclusions of the above cited review are listed below and followed by the petitioner's responses.

1. The summary sheets list the percentage of samples with residues ≥ 10 ppm and the average SO₂ level in a shipment. The overall range of residue levels should also be provided.

A total of 9659 samples were analyzed for SO₂ levels. Residues ranged from <0.03 to 72 ppm with a total of 2.74% having residues of 10 ppm or higher. The average exposure time, i.e., the number of days between the date the grapes were packed and the time the samples were taken, was 20 days.

2. Classification of residue samples with levels of SO₂ ≥10 ppm by pad manufacturer and also by grape variety² would provide significant comparative data. This should include the number of violative samples in the classification and the percent of violations as related to that particular group.

The petitioner states that over 99% of the grapes imported from Chile to the United States were packed with sulfiting pads manufactured by Uvas Quality, Osku-Vid, and Proem. The table below summarizes the residue data.

Pad Type	No. of Samples	Average SO ₂ Level	Percent ≥10 ppm
Uvas Qual.	6755	3.0	1.73
Osku-Vid	2089	3.9	3.76
Proem	639	4.5	5.88

Although the Uvas pads appear to have produced the lowest average SO₂ levels and the fewest samples with residues ≥10 ppm, the petitioner suggests additional factors which may have influenced these results. Certain importers had grape samples which were consistently lower in residues than other importers. In addition some importers used Uvas pads for most of the season, while others used Osku or Proem. To determine whether the lower residues with Uvas pads were due to the pads themselves or to the users, eight importers were identified who used approximately equal amounts of Uvas and Osku pads for the entire season. Although the residue levels observed from the use of Osku pads were higher than those obtained with the Uvas pads, the difference was not as great as in the table above. This suggests that the exporter's ability to control temperature and humidity while the grapes are packed, and the quality of the grapes, may be of more significance than the brand of pad used.

The 30 different grape varieties which were imported were broadly classified as seedless and seeded varieties. Approximately 90% of the grapes were seedless and consisted mainly of Thompson, Flame seedless and Perlette. Of the seeded varieties Emperor and Ribier accounted for the greatest volume. Seedless grapes tended to have higher residue levels than seeded grapes.

<u>Type of Grapes</u>	<u>No. of Samples</u>	<u>Average SO₂ Level</u>	<u>Percent ≥10 ppm</u>
Seedless	8504	3.4	2.91
Seeded	988	2.2	0.91

There was a clear difference in the SO₂ residue levels, with seedless varieties having significantly higher residues.

3. A comparison of recoveries obtained with different grape varieties and colors is needed. These data should help to determine whether there are significant differences in recoveries obtained with white and red grapes.

The question of potential variability in recoveries obtained using different grape varieties was not addressed. The petitioner states that these data are included in Exhibit 3 of this report. Exhibit 3 was not included with this report and may have been inadvertently omitted.

In the course of sample analysis, one spike recovery was run for every 10-20 samples, and only samples with a spike recovery of >70% were accepted as valid analytical results.

4. Significant differences were noted in the numbers of samples with residues greater than 10 ppm shipped into the three different ports, ie there appeared to be relatively fewer grapes with higher residues coming into Philadelphia than into Florida and California. The petitioner should determine whether these are real differences and to what they might be attributed.

Three major port locations were used in the United States, eastern (Philadelphia), western (Los Angeles), and southern (Tampa-Cape Canaveral).

<u>Region</u>	<u>No. of Samples</u>	<u>% ≥10 ppm</u>	<u>Exposure</u>
East	7057	1.22	21 days
West	2186	7.05	19 days
South	326	6.75	18 days

The western region had the highest percentage of violations. The petitioner feels that the higher residue levels in the Los Angeles area were due to the warmer southern California climate. In February and March ambient temperature in the Los Angeles area averaged 50-60°F, compared to 30-40°F in Philadelphia. In addition, grapes in Los Angeles were stored in a warehouse

without temperature control. Higher temperatures result in higher moisture and more release of SO_2 .

In southern Florida the average temperature was about the same as in California, however grapes were stored in refrigerated warehouses at about 33°F. Residues found in the samples from the southern area should have been less than what was actually found. The petitioner feels that the residues were higher than would be anticipated due to poor refrigeration on two of the vessels which went to Tampa throughout the shipping season, i.e., 20 out of 21 violations came from these vessels. One of these vessels which went to Los Angeles had 14 violations.

The petitioner further hypothesizes that the 2-3 day longer travel time to Philadelphia contributes to lower residue levels since the pads may be spent, giving the residues an opportunity to dissipate. While the first two theories appear to be likely contributing factors to the disparity in residue levels, the third is questionable. Data indicate that residue levels do not fall off significantly until after 4 weeks of exposure to the pads, i.e., inactivity of pads.

The study identified 8 vessels with residue levels significantly higher than the norm. Samples from the Savona Star, which had engine trouble and temperature control problems, were exposed to the pads for 31 days and had 4.55% samples ≥ 10 ppm. The other 7 vessels, with exposure time ranging from 16 to 23 days, had 10.00 to 23.08% of their samples ≥ 10 ppm. The petitioner feels that high residues were due to poor temperature control but does not have the records to prove it, since damage claims must be submitted against the shipping companies before such records may be obtained.

5. The petitioner has indicated that the information in this submission can be provided to EPA on floppy disc. The petitioner should submit a disc copy compatible with the IBM PC systems.

The petitioner has submitted the requested information on a floppy disc.

6. No information is provided concerning actual sampling techniques, storage of samples, analytical methodology and validation. We can draw no conclusions concerning the suitability of the subject residue data, for the purposes of registration, until these data are provided.

The registrant has provided detailed information concerning sampling, storage and analysis of samples.

When a ship arrived at a terminal, quality assurance/quality

control (QA/QC) personnel, based on the information provided by the importer, identified lots to be sampled and directed laboratory personnel to collect the samples for SO₂ analysis. Samples were collected in accordance to the FDA-approved protocol. Sample collections included one 500 gram sample from 5 different lugs of grapes from 5 different pallets within a defined lot. From December 1987 through February 18, 1988, samples were collected from a center bunch of grapes with approximately equal amounts of grapes plucked from top, middle and bottom of the bunch. After February 19, 1988, as mandated by FDA, samples were collected from grape bunches directly under the sulfiting pads. This biased sampling approach was intended to detect higher SO₂ residue levels, because grapes closest to the pad are expected to have the highest level of exposure to SO₂. The samples were then placed in coolers and packed with "blue ice" and transported to the laboratory for analysis.

The analytical method used for the testing of SO₂ levels in grapes was the official method, i.e., the FDA-modified Monier-Williams method. Whole grapes were used in the analysis, and the sample size was about 100 grams. One spike recovery was performed for every 10-20 samples, and only samples with a spike recovery of greater than 70% were accepted as valid analytical results.

When the analyses were completed, the results were transmitted by telefax to the importers' custom brokers who in turn transmitted the results to the district FDA. If the SO₂ levels were less than 10 ppm, the lots of grapes were released. If the results showed levels equal to or greater than 10 ppm, the lots were then segregated into wet and dry sublots (pads were wet or dry). The dry subplot could be resampled and retested. The wet subplot had to be reconditioned by removal of all SO₂ pads and aeration of the subplot for at least 48 hours before a resample and retest could be done.

The registrant identified 9 factors which appeared to contribute to variation in the SO₂ residue levels.

1. Port of entry - As discussed above, higher residues were observed in the western region than in the eastern and southeastern regions.
2. Location of piers - In the Philadelphia area, Pier 84 and Holt Terminal had lower residues than Tioga Terminal. This may have been due to the different importers which were using the locations rather than the locations themselves.
3. Date of arrival - There were a higher percentage of

samples in violation during the peak season. (Note that after 2/19/88 the FDA protocol was altered to require biased sampling.)

4. Importer - Depending upon the importer, different SO₂ residue levels were observed for the same variety of grapes shipped with the same brand of sulfite pad.
5. Pad type - Different residue levels were obtained using different brands of pads.
6. Condition of pad - If the lug contained a pad which was moist or wet the residue level was higher than if the pad was dry.
7. Variety of grapes - Seedless grapes contained higher residue levels than seeded varieties.
8. Exposure time - The average SO₂ levels were less with longer exposure time due to deactivation of the pad and depletion of residues.
9. Shipping vessel - As discussed above, samples from certain shipping vessels had unusually high residues.

In the petitioners' opinion the most important of the above factors was the condition of the pads and the exposure time.

Condition of Pads

Each pad contained 5.0 to 7.2 grams of sodium metabisulfite, depending upon the pad manufacturer. The average SO₂ level for wet lug designation was the highest of any of the sorted variables.

<u>Lug Condition</u>	<u>% Samples</u>	<u>% ≥10 ppm</u>	<u>Exposure</u>
Wet	0.72	7.46	17 days
Moist	19.5	5.04	19 days
Dry	79.8	2.26	20 days

There is a clear correlation between the condition of the pad and the residue levels, with grape samples associated with moist or wet pads containing much higher residues than those packed with dry pads.

Exposure Time

Shipping time from Chile is 12 to 14 days. The minimal exposure time to the pads is 12 days, with 21 days the more

typical time frame. Some grapes were exposed to the pads for as much as 60 days. The highest number of violations occurred with exposures of 19.1 to 24.1 days, ranging from 3.00 to 5.25% of the total samples. No violations were found after 32 days. Data indicate that SO₂ levels will increase with sustained exposure to pads in the initial period, and may decrease after 21 days if the pad becomes exhausted or inactivated at the end of this time period.

The petitioner has adequately addressed the questions raised in our September 22, 1988 review, "Sulfur Dioxide on Grapes; Data from Chilean Certification Program" (Elizabeth T. Haeberer).

cc: RF, Circu, E. Haeberer, PP#7E3473, FDA, PMSD/ISB
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